Journal Pre-proof

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PII: S0048-9697(20)32992-2

DOI: https://doi.org/10.1016/j.scitotenv.2020.139475

Reference: STOTEN 139475

To appear in: *Science of the Total Environment*

Received date: 19 February 2020

Revised date: 13 May 2020

Accepted date: 14 May 2020

Please cite this article as: J. Potapowicz, D. Lambropoulou, C. Nannou, et al., Occurrences, sources, and transport of organochlorine pesticides in the aquatic environment of Antarctica, *Science of the Total Environment* (2020), https://doi.org/10.1016/j.scitotenv.2020.139475

Occurrences, sources, and transport of organochlorine pesticides in the aquatic environment of Antarctica

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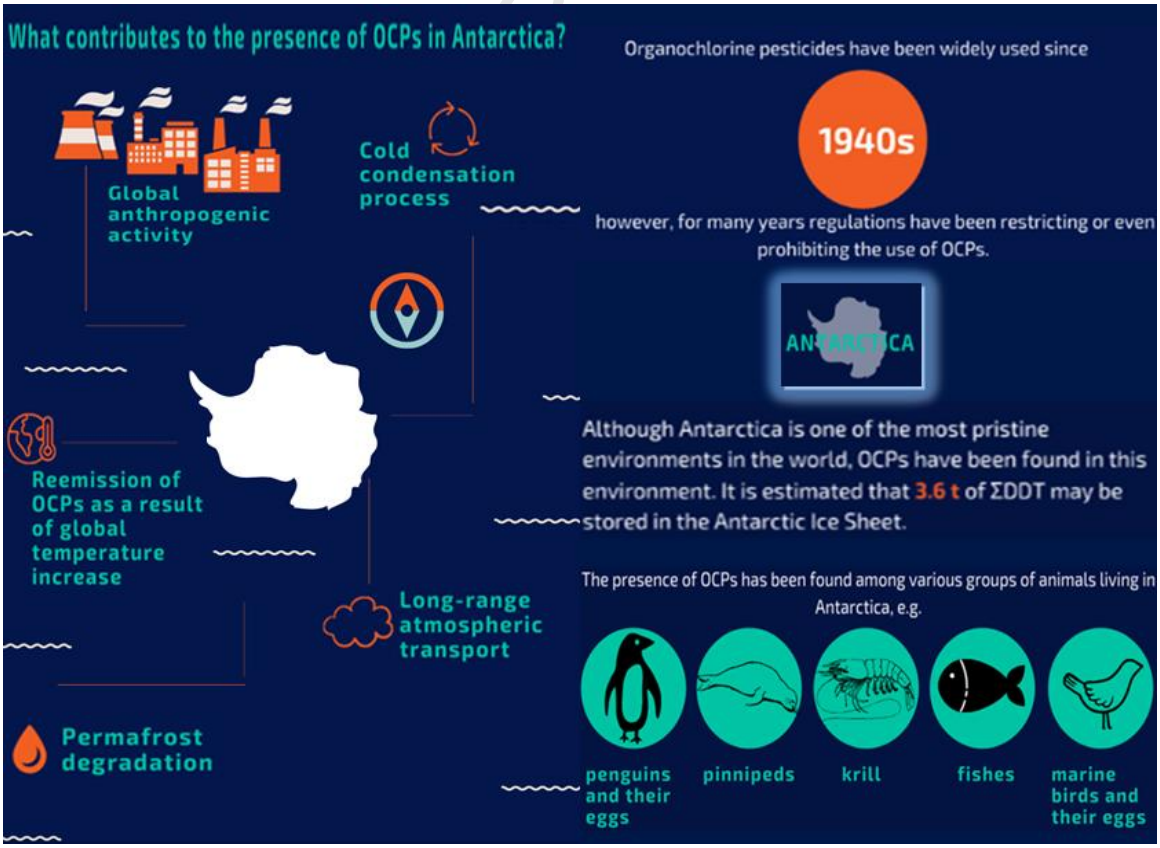
Graphical abstract



Abstract

We review information on the concentration levels of organochlorine pesticides in the abiotic aquatic environment (in seawater, sea ice, surface freshwater, snow, firn, and glacial ice) and the organisms inhabiting those, in Antarctica. Particular attention is given to the environmental fate of these pollutants, which modifies their impact on the organisms living in the Antarctic. OCPs have been delivered to the Antarctic environment mainly via long-range transport from inhabited areas, and due to their long accumulation they are sometimes reemitted from melting cryosphere. Since climate change is forecasted to intensify, the release of anthropogenic pollutants from increased seasonal thaw may prove its importance for the future state of this unspoiled environment. However, the limited estimations of the OCPs storage magnitude in the Antarctic cryosphere are relatively crude and may err significantly towards higher values. The OCPs are already present in different types of animal tissues at every trophic level, where they may cause negative effects such as reproductive disorders, decreased survival rates, and an increased parasitic load. Therefore, it is important to continuously monitor OCP concentrations in various elements of the Antarctic environment and the fate of these pollutants, taking into account their global and local sources, including the remobilization from frozen state.

Keywords: organochlorine pesticides, pollution remobilisation, anthropogenic influence, environmental threat, Antarctica

Highlights:

- OCPs in the Antarctic come from distant anthropogenic activity
- Melting ice plays an important role in the fate of OCPs in the Antarctic environment
- The presence of OCPs causes multiple negative effects on Antarctic fauna

1. Introduction

The ecosystem in Antarctic waters is uniquely adapted (Cavicchioli, 2015) and globally relevant for primary productivity (Dierssen et al., 2000). While Antarctica is one of the most pristine environments in the world (Ainley, 2007), the aquatic organism there are still exposed to pollution. The effects of human activities can be observed in the Antarctic environment (Gao et al., 2018; Geisz et al., 2008;

Tanabe et al., 1983), such as the footprint of tourist and research station activities (Szopińska et al., 2018; Harcha, 2006). In the recent decades, there has been a rapid increase in global pollutant emissions in general, which contributed to their distribution across the global environment (Cipro et al., 2013; Yadav et al., 2017; Ma et al., 2017; Potapowicz et al., 2019). Unfortunately, this global trend affects even the Antarctic environment, requiring more and more of the global scientific community (Möller et al., 2012; Cincinelli et al., 2016; Vecchiato et al., 2015a). As a result of the global anthropogenic activities, an accelerated warming and other climatic changes have been observed in the Antarctic (Kejna et al., 2013; Szopińska et al., 2018). As a result of these changes, an increased transport of pollutants from urban areas due to air mass movement was observed (Corsolini, 2009; Bengtson Nash, 2011) and reemission of pollutants from permafrost to the Antarctic environment has also been considered in this area (Szopińska et al. 2018). The most frequently raised issue by scientists is the increase in trace metals concentrations in this area (e.g. Abakumov et al., 2017; Lu et al., 2012; Santos et al., 2005; Szopińska et al., 2018; Tin et al., 2009). It was found that the concentrations of persistent organic pollutants (POPs) increase in biological tissues collected in Antarctica.

A particularly long-standing threat among the POP compounds detected in Antarctica are organochlorine pesticides (OCPs) (Cipro et al., 2017; Bigot et al., 2016a). Since the 1940s, these compounds have been widely used, mainly in agriculture. However, for many years, regulations have been restricting or even prohibiting the use of OCPs. One of them is the Stockholm Convention, adopted by the United Nations Environment Program. Legislation largely protects the environment against increased OCPs in the environment, but not all countries comply with these bans. In addition, OCPs are resistant to environmental degradation processes (Bigot et al., 2016b).

In general, OCPs have been transported from populated areas to the Antarctic by long-range atmospheric transport (LRAT), where their further movement has been restricted by the cold conditions (Bigot et al., 2016b, Geisz et al., 2008). As a result, OCPs were deposited in snow and ice; afterwards, melting, especially the release of particulate organic matter from the ice, feeds them into the base of the food web (yet a proportion of the released OCPs may come back to the atmosphere through volatilisation)(Chiuchiolo et al., 2004). During circumpolar long-term research in the Antarctic over the last several decades, climate change and the resulting melting and retreat of

Antarctic ice shelves was observed (Vaughan et al., 2003; Turner et al., 2005; Mulvaney et al., 2012; Kejna et al., 2013). Ducklow et al. (2007) showed that regional climate warming correlates with ecosystem changes throughout the sea-ice dominated areas of the Western Antarctic Peninsula. In addition, Bogdal et al.(2009) have observed (in the European Alps) that pollutants may be secondarily input to the environment through glacier melt, while Bigot et al., 2016b confirmed their presence in Antarctic ice cores. Particularly noteworthy is the fact that it may come to the possible future reemission of OCPs, among other POPs, into the atmosphere and surface waters. These chemical compounds have accumulated in the Antarctic over the years in the ice layers corresponding to the pollutant emission period.

OCPs, considered the typical persistent toxic substances (PTS), deserve special attention because of their persistence, bioaccumulation, and toxicity (Chopra et al., 2011; Willett et al. 1998; Quan et al. 2003; Wong et al. 2004). The presence of OCPs in the Antarctic environment was reported for the first time in the 1960s (Sladen et al., 1966; George and Frear, 1966). In the 12th Stockholm Convention, eleven OCPs were proposed to be controlled because of their harmful effects to the environment and ecosystems (Chopra et al., 2011; Bigot et al., 2016b), including dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), pentachlorobenzene, chlordane, dieldrin, endrin, heptachlor, mirex, toxaphene, hexachlorocyclohexane (alpha-HCH, beta-HCH, and gamma-HCH, also named lindane, and chlordecone, while endosulfan has recently been proposed to the European Union to be included under the provisions of the above-mentioned Convention. Despite the introduction of bans and restrictions on the use of OCPs, many research groups showed that these compounds occur both in the Antarctic aquatic environment and in the trophic networks of organisms living in this area (Chiuchiolo et al., 2004; Dickhut et al., 2005; Inomata et al., 1996; Sun et al., 2006; Taniguchi et al., 2009; van den Brink, 1997).

The toxic effects of OCPs on biota are known, as detailed in publications on the areas with more intensive human activity (Agnihotri et al., 1994; Bai et al., 2018; Barhoumi et al., 2014; Carlson et al., 2004, Carro et al., 2017; Petrovic et al., 2018). In the case of ecosystems found in Antarctica, the fate of these compounds is also affected by the low temperature conditions (Zhang et al., 2009). Lipophilic OCPs accumulate in the fat tissue of biological organisms and can be biomagnified, which

poses a risk to organisms of higher trophic levels. For example, Jara-Carrasco et al. (2015) proved that significant concentrations of HCB, DDT, α-endosulfan, β-endosulfan in tissues of Chinstrap penguin (*Pygoscelis antarctica*) can result in adverse changes, such as decreased reproductive success, increased risk of parasitism, greater wing asymmetry and immunohematological disorders. There are many studies regarding OCPs concentration levels in penguin and pinniped mammals' tissues, as well as on the impact of these compounds on life processes (George and Frear, 1966; Schiavone et al., 2009; Sun et al., 2006). Research on the determination of OCPs in aquatic organisms that are at the beginning of the trophic chain, e.g. the Antarctic krill, is also warranted by their multiplied impact on the higher trophic levels (Cipro et al., 2013; Goerke et al., 2004).

Considering that OCPs are bioaccumulated in the tissues of living organisms at different trophic levels, it is important to compare the concentrations of these chemical compounds in various animal tissues, as well as to determine the impact of OCPs on the Antarctic biota. This work is an attempt to compile the existing knowledge on the status of these chemicals in the aquatic environment of the Antarctic, taking into account both the abiotic background concentrations and the aquatic or semi-aquatic animals. While the comparison of OCP concentrations in these two elements of the Antarctic environment has been missing in the previous work, it may be important for understanding the exchange of these compounds to and from the Antarctic ecosystem, and learning about the processes occurring in this polar environment. Special attention has been paid to the different sources of these compounds (anthropogenic, local or long-distance) and the environmental fate of pollutants. The proposed review will also contribute to assessments of the potential environmental hazards associated with the accumulation of OCPs in the Antarctic environment.

2. Sources and the deposition of organochlorine pesticides in Antarctica

Organochlorine pesticides are widespread contaminants in many environments around the world, including the polar regions. Studies over the years have shown that OCPs are detected in the Antarctic air (Kang et al., 2012), water (Cipro et al., 2017), soil (Zhang et al., 2015) and biota (Schiavone et al., 2009). The presence of OCPs in this region has been attributed to cold condensation and global fractionation during the long-range atmospheric transport (LRAT) (Wania and MacKay, 1996). In

addition, local impact on the increase of environmental pollution in latitudes over 62°S is also observed (Evenset et al., 2007; Roosens et al., 2007).

In a description of the environmental fate of OCPs in polar environments, one cannot ignore the impact of the cold trap effect. This phenomenon is characterized by the transport of chemical compounds in the atmosphere, caused by a decrease in temperature and resulting in the deposition of these compounds. It has been shown that despite the highest POPs emission at temperate and tropical temperatures, these pollutants do not remain there: a proportion of their chemical load volatilizes and then moves through the atmosphere, to be later condensed at colder, higher latitudes (Wania and Mackay, 1993, 1996; Dickhut et al., 2005). Cycles of long-range atmospheric transport, deposition and reemission (Rappe, 1974; Goldberg, 1975) can be repeated many times which makes them a source of pollution in areas with insignificant anthropogenic activity, such as Antarctica, leading to the accumulation of these compounds (Wania and Mackay, 1993, 1996; Jones and Voogt, 1999). The transport of pollutants in the atmosphere has a significant impact on the pollution load in the hydrosphere (Bidleman, 1999). In addition, Galbán-Malagón et al. (2013) showed that in the Antarctic environment, the biological degradative processes in water may result in disequilibrium in atmospheric and aquatic concentrations of OCPs, driving the absorption of HCHs and HCB through air-to-water fluxes.

One of the important aspects affecting the presence and spread of OCPs in polar environments is global climate change. These processes affect the transport and redistribution pathways of POPs (Kalleborn et al., 2012; Kosek et al., 2018). It is caused by the dependence accumulation, reactivity and adsorption processes are temperature dependent (Kalleborn et al., 2012). Glaciers are an important component of the Antarctic and Arctic regulating water circulation in the cold environments. They are characterized by the fastest and strongest respond to climate changes (Lehmann et al., 2016). Global warming can cause the release of accumulated quantities of OCPs in glacial ice, which will result in the increase the loading of these pollutants in glacial-fed systems (Weber et al., 2010). Many physical and chemical properties of POPs provide information regarding their presence and distribution in the environment (Kosek et al., 2018). In addition, the values of some of them, e.g. a chemical's vapor pressure, Henry's law constant, the air-water partitioning coefficient and the octanol-air partitioning

coefficient are related to the temperature value (Kalleborn et al, 2012). While seasonal changes in air temperature do not drastically affect the properties of chemical pollutants, so many years of climate change over the decades can contribute to drive phase partitioning of semi-volatile chemicals towards the gas phase (Kalleborn et al, 2012). The consequence of this may be an increase in the translocation of chemical compounds in the environment, thereby increasing the extent of pollution.

It has been observed that snow can be a seasonal secondary source (Fig.1) of OCPs in Antarctica (Kallenborn et al. 2013). This phenomenon is particularly relevant to lighter and more hydrophilic compounds (Muir and Lohmann 2013). Falling snow removes OCPs from the atmosphere through washout of atmospheric aerosols and absorption of their vapors (Kang et al., 2012). Therefore, the accumulation of these compounds in the environment is promoted, affecting their further fate (Daly and Wania, 2004; Stocker et al., 2007). Despite their lipophilic nature, OCPs are accumulated in the snow and ice, constituting a reservoir of these compounds. Due to their lipophilic character, on the other hand, they are capable of bioaccumulation and further adverse effects on fauna (Chopra et al., 2011; Geisz et al., 2008). During their research, Cipro et al. (2017) observed that as the general sum of the OCP concentrations decreases during the austral summer season, proportionally the concentrations in snow remain higher than in snow meltwater. This can be caused by the non-linear redistribution of the compounds between these two phases (Gross et al., 1977). In addition, OCPs may enter a new state of equilibrium, reevaporate or be adsorbed to organic matter after entering the liquid phase (Wania, 1997).

The flow of pollutants from melting glaciers also affects the surface water OCP concentrations (Blais et al. 2001; Li-guang et al., 2005), and ice can be a vast reservoir of OCPs. It is estimated that 3.6 t of ΣDDT may be stored in the "Antarctic Peninsula ice sheet" (Geisz et al., 2008), yet the estimation seems to apply the average concentration of the pollutant in the top 6 m of snow to the whole ice sheet thickness (averaged as 1780 m), which is an obvious misrepresentation of the period when this contaminant was deposited. Thus, most likely, the storage of the pollutant in the ice sheet has been much lower than estimated. It should also be decreasing where glaciers experience surface ablation. Ducklow et al. (2007) noticed a 6°C-increase in the mean winter temperature, while the annual mean temperature increased by 2^{o}C on the Antarctic Peninsula from 1950. In addition, the ice

volume loss, glacier retreat and meltwater production have also increased (Cook et al., 2005). The conditions described are conducive to the release of pollutants accumulated in ice, which is confirmed by research on the concentrations of selected compounds in glacial runoff (Chiuchiolo et al., 2004).

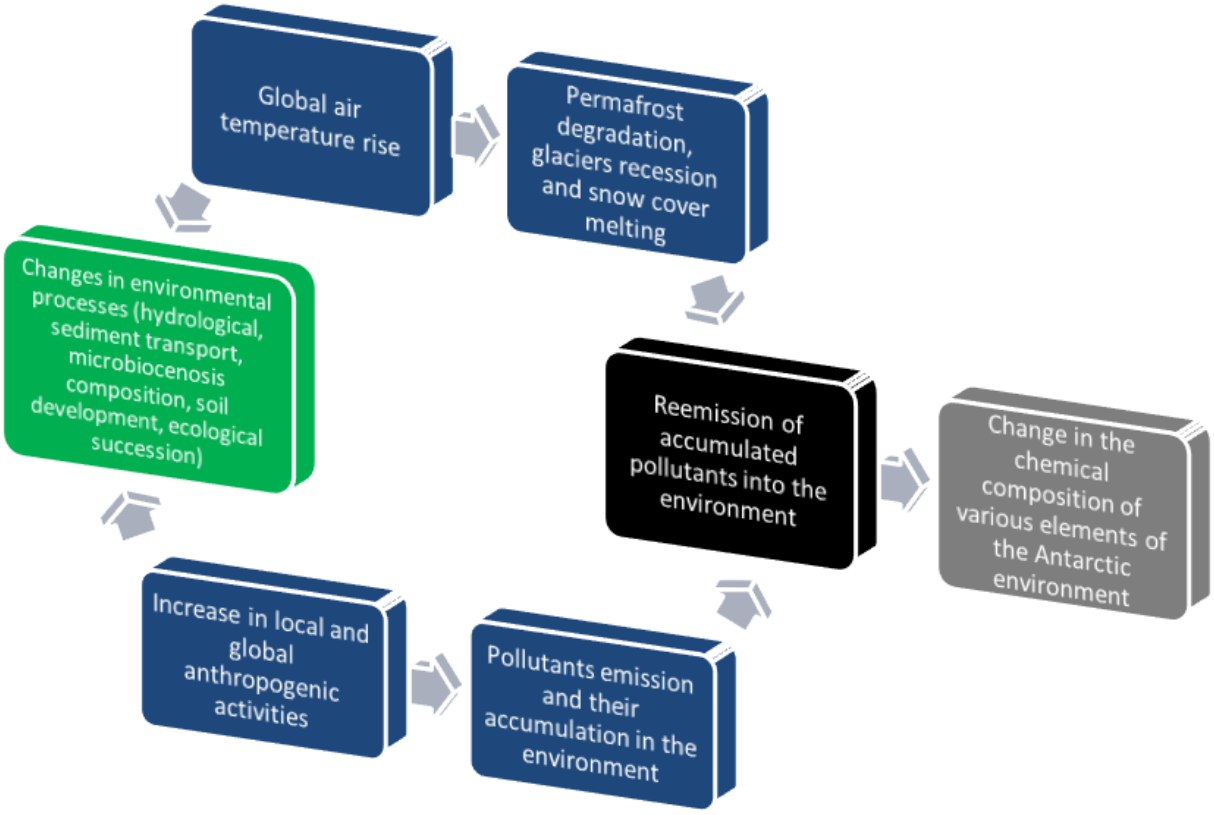


Figure 1. A diagram of the secondary release of OCPs in Antarctica.

It is believed that the inflow of pollutants to the Antarctic Peninsula is strongly limited by the range of circumpolar air circulation (Szopińska et al., 2018), yet small concentrations of pollutants are delivered to the interior of Antarctica. The redistribution of such pollutants is affected, among other factors, by wind speed and direction. Mishra et al. (2004) drew attention to the long-range atmospheric transport of metallic compounds identified in the air at the King Sejong Station (King George Island, South Shetlands Islands). In addition, Kallenborn et al. (2013) observed the same effect in the case of POPs on Dronning Maud Land, and Lee et al. (2004) with reference to volcanic ashes from Patagonia in the soil of the Barton Peninsula. Szopińska et al. (2018) analyzed the wind directions at King George Island in 2016, based on the data from Bellingshausen station. The authors concluded that predominant wind directions are north-westerly (30% - NNW, NW, WNW) northerly (10% - N),

north-easterly (9% - NE) and south-easterly (8% - SSE). Furthermore, it was observed that the dominant wind direction also changes depending on the season (Fig. 2).

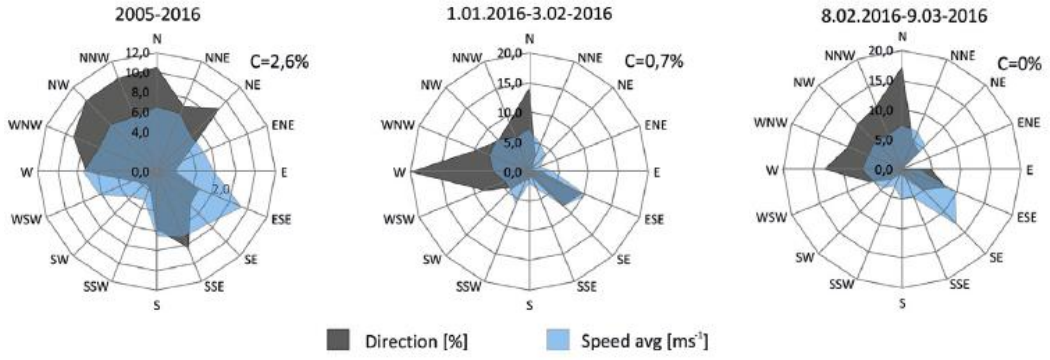


Figure 2. Wind directions and wind speed in the period of 2005–2016 at the Bellingshausen Station (King George Island, Maritime Antarctica) (Szopińska et al., 2018).

The Southern Hemisphere atmospheric circulation transports pollutants from populated emission areas to the Antarctic, where they are deposited (Russell and McGregor, 2010), e.g. with snow, and remain due to cold condensation (Wania and Mackay, 1993). While the degree of pollution in the Antarctic Peninsula may have a direct connection to Argentina and Chile (Dickhut et al., 2005), in remote regions of Antarctica it has been suggested that a potential secondary source can be also the wind ventilation of snow (Kang et al., 2012). However, as the air masses travel a long way into the Antarctic continent, their pollutant load becomes more diluted in the atmospheric air and, consequently, the inland areas experience lower levels of OCPs in snow than the Antarctic coast (Kang et al., 2012). Bigot et al. (2016a), who compared OCP concentrations in air and seawater at points located across the Southern Ocean, also found them diminishing with increasing latitude. Finally, local orographic conditions modify the level of contamination (Kejna et al., 2013).

3. Levels of organochlorine pesticides in the aquatic environment and fauna in Antarctica

OCPs have been found even in as pristine an environment as Antarctica. Table 1 presents the published data on the concentrations of selected OCPs in the aqueous abiotic environment of Antarctica in relation to geographical location, type of matrix (water, snow, ice), water salinity (seawater and freshwater) and sampling year.

In the water and snow all the determined compounds from the OCP group chosen for this review were found, i.e. dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), drins (aldrin, dieldrin, endrin and isodrin), chlordanes (α- and γ-chlordane, oxychlordane, heptachlor epoxide). Ice samples were characterized by significant concentrations of HCHs and chlordanes (Dickhut et al, 2005). DDTs and HCHs were the most common OCPs in all environmental samples. Based on the literature (Table 1), it can be concluded that the concentration levels of selected OCPs in various elements of the Antarctic environment were relatively low (usually at 1 - 600 pg/L level), most likely due to the large distance from densely populated areas and the geographical barrier (the ice barrier of Antarctica) hindering the transport of pollutants. In addition, Figure 3 shows the location of research areas in Antarctica, where selected OCPs have been determined in water, ice and snow.

In the case of freshwater, the highest concentrations of DDTs, chlordanes and drins were found in waters originating from a lake on King George Island (Gao et al., 2018). ∑OCPs in this lake water reached concentrations of to 0.33 ng/l in one sample. The authors claim that such high concentrations of OCPs there result from the relative proximity of lower latitude emission areas. This explanation aligns with the observation of Bigot et al. (2016a), that the concentration of some OCPs in the oceans decreased with latitude. Furthermore, in the King George Island area, the lake water concentration of DDTs, chlordanes and drins exceeded those in seawater. This fact may be explained by a continuous accumulation of pollution in the lake without drainage and the slow processes of neutralising such pollution. In particular, the extra load of organochlorine pollutants entering the lakes (and the sea, in a more dilute form) may come in the cold climate from melting snow and ice covers (Cabrerizo et al., 2019). As for HCHs in freshwater, their highest concentration levels were found at Lake Nurume near Syowa Station (Tanabe et al., 1983). The station is located on East Ongul Island in Queen Maud Land, Antarctica. The authors claimed that the source of DDT and HCH was in the developing countries in the tropics (via long-range transport), which at the time used these pesticides in large quantities. In addition, Lake Nurume is located at a relatively low latitude, which increases the pollution inflow.

The concentrations of OCPs in seawater are typically lower than in freshwater, yet this pattern did not occur for HCHs near Syowa Station (Tottuki Point, Kitano-ura Cove) (Tanabe et al., 1983) and HCB in the western Ross Sea (Cincinelli et al. 2009) and in the Southern Ocean (Bigot et al., 2016a). These points are located on opposite ends of the Antarctic. Cincinelli et al. (2008) stated that the high OCPs concentrations may result from their inflow from melting sea ice and snow, and the decrease in HCB in the spring may be the result of bioaccumulation in phytoplankton, as well as to volatilization due to HCB high vapour pressure. The latter explanation appears more likely, as Chiucholo et al. (2004) report no bioaccumulation or biomagnification of HCB at the lowest levels of the Antarctic food web (ice algae and krill).

In snow and ice, the concentrations of selected OCPs are higher than in freshwater and seawater. However, polynya water (Sen Gupta et al. 1996) exhibited notably higher concentrations than seawater in general, as well as sea ice (Dickhut et al, 2005), and effect which Pućko et al. (2015) attribute to enhanced dry deposition of OCPs in these melt ponds. Particularly noteworthy are again snow and ice samples taken near Syowa Station (Tanabe et al., 1983), which were characterized by many times higher HCHs concentrations than in other places in Antarctica. For these and other matrices, the high concentrations may be connected to the year when the samples were collected. Since then, the use of OCPs has been significantly reduced due to their harmful environmental impacts. The highest concentrations of DDTs, drins and chlordanes in snow and ice were found in the King George Island area, near Brazilian Research Station Feraz (Cipro et al., 2017). The authors point out the possible cause of differences in OCP concentrations between water and snow/ice, which is that during melt this class of pesticides can be lost through volatilisation or adsorption on organic matter. Furthermore, their elution pattern during snow melt may concentrate them at certain times, as opposed to relative dilution at other – e.g. for lindane (γ-HCH), the concentration is enhanced at the beginning and the very end of snow melt (Meyer and Wania, 2011).

Table 1. The total dissolved concentrations of OCPs in water, snow, and ice, at various sampling sites.

TYPE OF SAMPLE	LOCATION	DDTs[a]	HCHs[b]	HCB	Drins[c]	Chlordanes[d]	Unit	Reference
freshwater	Lake Nurume	1.3	330	-	-	-	pg/L	(Tanabe et al., 1983)
	Brazilian Research Station Feraz, King George Island	4.32-6.30	2.06-3.14	1.76-2.47	<0.35-2.73	5.72-7.48	pg/kg	(Cipro et al., 2017)
	Lake on King George Island	<LOD-0.073	-	-	<LOD-0.11	<LOD-0.33	ng/L	(Gao et al., 2018)
polynya water	Dakshin Gangotri	24.8-26.5	85.6-90.7	-	-	-	pg/L	(Sen Gupta et al. 1996)
seawater	western Ross Sea	-	0.61-8.79	1.72-16.24	-	-	pg/L	(Cincinelli et al. 2009)
	Tottuki Point	1.3	570	-	-	-	pg/L	(Tanabe et al., 1983)
	Langhovde	1.5	210	-	-	-		
	Kitano-ura Cove	1.5	570	-	-	-		
	Southern Ocean (Weddell, South	-	0.189±0.09-3.132±4.031	0.281±0.078 –	-	-	pg/L	(Galbán-Malagón et al 2013a)

TYPE OF SAMPLE	LOCATION	DDTs[a]	HCHs[b]	HCB	Drins[c]	Chlordanes[d]	Unit	Reference
	Scotia, and Bellingshausen Seas)			0.976±0.828				
	Dakshin Gangotri	0.63-4.27	-	-	-	-	pg/L	(Sen Gupta et al. 1996)
	King George Island	<LOD-0.044	-	-	<LOD-0.42	<LOD-0.49	ng/L	(Gao et al., 2018)
	Palmer Station	-	2.7-15.04	-		-	pg/L	(Dickhut et al, 2005)
	Southern Ocean	0.59-5.61	<2.96-7.67	2.59-4.14	<0.65-1.43	<0.17-0.44	pg/L	(Bigot et al., 2016a)
snow	Dome Fuji, East Antarctica	-	17.5-137.0	<LOD-182	-	-	pg/L	(Kang et al. 2012)
	Mizuho Station	15	2300	-	-	-	pg/L	(Tanabe et al., 1983)
	Tottuki Point	17	2800	-	-	-		
	Lake Nurume	16	4900	-	-	-		
	Brazilian Research Station Feraz, King George Island	5.3-24.4	1.46-4.17	1.36-3.77	<0.35-4.29	11.39-13.3	pg/kg	(Cipro et al., 2017)

TYPE OF SAMPLE	LOCATION	DDTs[a]	HCHs[b]	HCB	Drins[c]	Chlordanes[d]	Unit	Reference
	Palmer Station	-	3.17-8.91	-	-	<LOD-7.82	pg/L	(Dickhut et al, 2005)
ice cover	Tottuki Point	11	2200	-	-	-	pg/L	(Tanabe et al., 1983)
	Lake Nurume	9.8	2000	-	-	-		
sea-ice	Palmer Station	-	5.24-7.46	-	-	<LOD-8.02	pg/L	(Dickhut et al, 2005)
porewater in sediments	Western Antarctic Peninsula	0.11-1.00	-	0.63-6.7	-	-	pg/L	(Zhang et al. 2013)

[a] DDTs : p,p'-DDE; o,p'-DDT; p,p'-DDD; p,p'-DDT

[b] HCHs: α-HCH; β-HCH; γ-HCH

[c] Drins: aldrin, dieldrin, endrin and isodrin

[d] Chlordanes: α- and γ-chlordane, oxychlordane, heptachlor, and heptachlor epoxide

LOD- limit of detection

Table 2 presents a literature review of the concentrations of selected OCPs in Antarctic biota, with respect to the type of sampled tissue, sample collection year, animal species, and trophic level. Figure 3 shows the spatial distribution of research areas, where selected OCPs have been determined in Antarctic fauna. The highest concentrations of DDTs and endosulfans were found in penguin blood, in samples from Kopaitic Island and in the area of Cape Shirreff, respectively (Jara-Carrasco et al., 2015). The highest level of HCB concentration was found in the area of Lenie Field Station on King George Island (Corsolini et al., 2007). Jara-Carrasco et al. (2015) showed that differences in the concentration of selected OCPs in the blood of individual species of penguins may be due to the differences in their diet and their migration behaviour exposing them to varying concentrations of these pollutants at different times of the year. Furthermore, it has been suggested that the presence of endosulfans in Antarctica can be caused by the intensive use of insecticide in South America, especially in Argentina (Pérez et al. 2013). Both the production and the use of this insecticide have been banned relatively recently, in July 2013. Finally, attention should be paid to the geographical location of the points with the highest concentration of OCPs in penguin blood. These were all located in the vicinity of South Shetland Islands or South Orkney Islands. These islands are exposed to the largest inflow of pollution from densely populated areas.

OCPs have also been found in penguin fat and liver. Tatton and Ruzicka (1967) wrote about DDTs content in tissues at the level of 0.002-0.059 mg/kg, which represents a low concentration compared to the study of Taniguchi et al. (2009), who found concentrations higher by an order of magnitude. The difference in concentrations may result from the time dividing both studies, both in the context of continuous bioaccumulation of these pollutants and the accuracy of measuring apparatus, which could prevent the detection of some OCPs and thus lowered the sum of the individual chemical compounds concentrations.

The OCPs concentrations in adipose tissue of other birds depend strictly on the species, likely in connection to their dietary preferences. The content of DDTs was lower in 1967 than in 2009, in the fat of not only penguins, but also other bird species (e.g. brown skua, blue-eyed shag, antarctic tern and snowy sheathbill) (Tatton and Ruzicka, 1967; Taniguchi et al., 2009). Furthermore, HCHs were several times more concentrated in other birds than penguins (Taniguchi et al., 2009). It was also

found that brown skua fat had higher concentrations of HCB than penguin and other bird species fat, which may be due to the fact that brown skua is at a higher trophic level. Finally, significant concentrations of DDTs, HCHs, and drins, have been found in various sections of the penguin digestive tract. The concentration of these OCPs ranged from 1.49 to 2.67 ng/g in the case of droppings (Sun et al., 2006), while in stomach contents it was approximately 1 ng/g (Tatton and Ruzicka, 1967).

Schiavone et al. (2009) compared the content of selected OCPs in eggs of three penguin species and found the lowest DDTs and HCB values in gentoo penguin eggs which contained 3.7 ng/g HCB and 15 ng/g DDTs. Concentrations in chinstrap penguin eggs were slightly higher (3.8 ng/g HCB and 17 ng/g DDTs), while the Adélie penguin eggs exhibited the highest levels (7.63 ng/g HCB and 23 ng/g DDTs). Since these species live in the same area, the differences in chemical concentrations may be ascribed to factors such as diet, reproductive status, ecological niches, and migration behaviour. Hence the eggs of different bird species can provide information on the degree of the species exposure to OCPs. For example, the HCB concentrations in the eggs of south polar skua and three species of penguins indicated a decrease with increasing trophic position (Mello et al., 2016). The levels of DDTs in south polar skua eggs were many times higher than in the case of penguin eggs, which indicates a high exposure of south polar skua to this pollutant class.

Pinnipeds are a common group of animals on the Antarctic coasts and islands. The OCPs content in their adipose tissue varies between the species, for example in connection to their dietary preferences. Southern elephant seal fat samples from Elephant Island were characterized by the highest concentrations of DDTs among other pinnipeds species (187.72 ng/g, lw) (Miranda-Filho et al., 2007). This value was similar to the content of these compounds in pinniped fat from King George Island (Cipro et al., 2012), which ranged from 14.4 to 168 ng/g lw, depending on the species. The highest concentrations of chlordanes and HCB were found in Weddell seal fat, which were 37.87-106.17 and 94.57-340.66 ng/g lw, respectively (Vergara et al., 2019). On the other hand, Crabeater seal blubber contained the most HCHs (75.70-111.15, ng/g lw) (Vergara et al., 2019). Both the latter pinniped species with the highest concentrations of the mentioned OCPs originated from the vicinity of Cape Shirreff Field Station (Livingstone Island). However, when Schiavone et al. (2009) also

determined the concentrations of DDTs and HCB in the antarctic fur seal blubber living on Livingstone Island, they obtained values below the detection limit. On the other hand, the highest concentrations of endosulfans (21.15 ng/g, lw) and drins (82.4 ng/g, lw) occurred in the antarctic fur seals from King George Island (Schiavone et al., 2009).

The OCP concentrations in the liver of Southern elephant seal and Antarctic fur seal also differed: in favour of the Antarctic fur seal in the case of DDTs concentrations, and in favour of the Southern elephant seal for HCB (Cipro et al., 2012; Schiavone et al., 2009). The Southern elephant seal liver was also found to contain 1.41, 6.88, 2.72 and 37.7 ng/g lw of HCHs, drins, endosulfan and chlordanes, respectively (Cipro et al., 2012). The concentration of DDTs in Antarctic fur seal muscle (103 ng/g, ww) was similar to that in Southern elephant seal liver (98.7 ng/g, lw), and HCB concentration on those samples was lower than in the liver of both species (Cipro et al., 2012; Schiavone et al., 2009).

Significant concentrations of selected OCPs were also found in the aquatic organisms which for the most part constitute food for the animals described above. This shows that OCPs can be found at the lower levels of the food chain, too. Lana et al. (2014) determined the sums of OCPs in muscle, liver, gonads, and gills of fishes. The authors found the highest concentrations of DDTs in Notothenia rossii fish (253.6 ng/g, lw), and of HCHs in the Notothenia coriiceps fish species (61.02 ng/g, lw) (Lana et al., 2014). Furthermore, the concentrations of other OCPs in the aquatic organism tissues were also determined in other locations (Cipro et al., 2013; Strobel et al., 2018), and the highest concentrations of HCB (8.56 ng/g ww), drins (1.11 ng/g, ww) and chlordanes 3.94 (ng/g,ww) were found in the samples of Nacella concinna soft tissue. Finally, endosulfans peaked in Notothenia spp. muscle (Cipro et al., 2013).

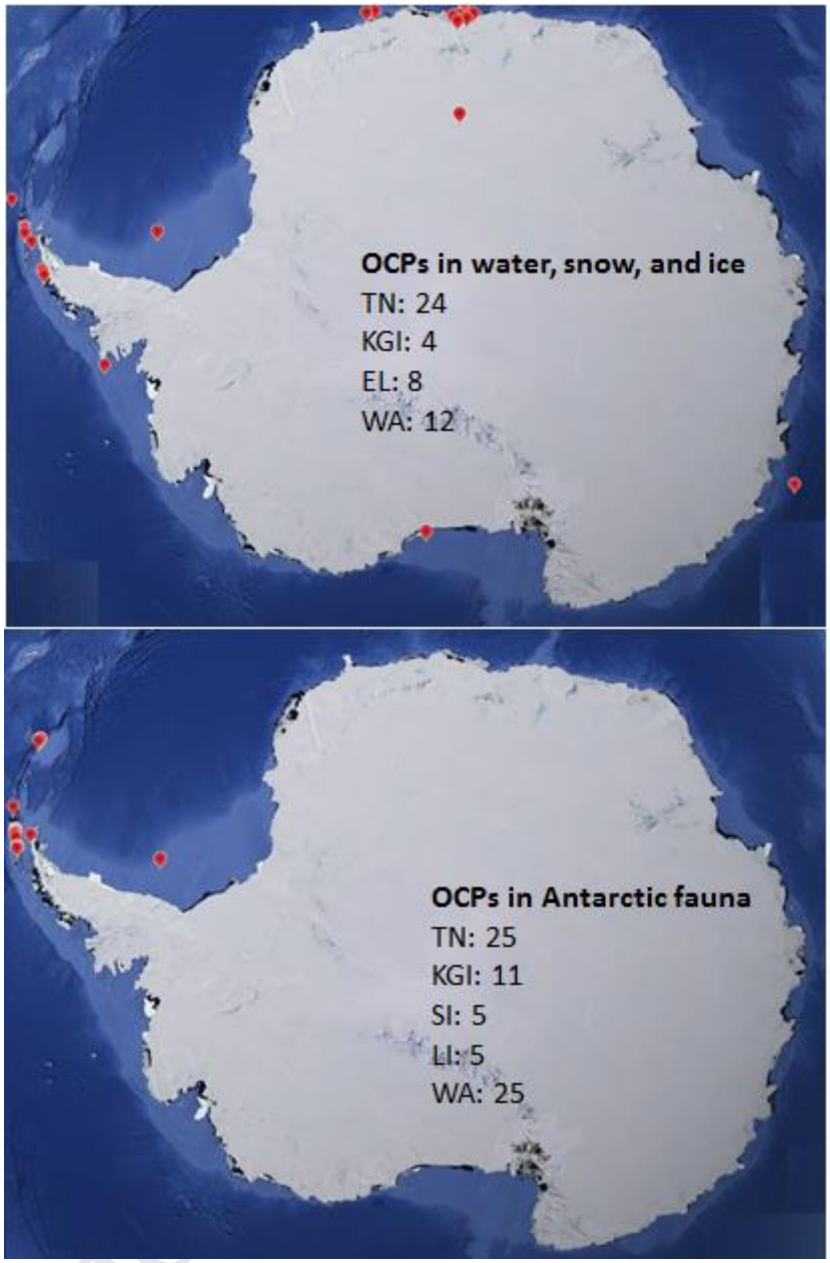


Figure 3. Location of research areas in Antarctica, where selected OCPs have been determined in aquatic and biotic samples. Abbreviation: TN – total number of researched points, KGI – number of researched points in King George Island, LI – number of researched points in Livingstone Island, EL – number of researched points in Enderby Land, EL – number of researched points in Signy Island, WA – number of researched points in western Antarctica. Maps have been prepared based on results obtained by articles in Table 1 and 2. The maps were made using https://earth.google.com/.

Table 2. The concentrations of OCPs in Antarctic fauna at different sampling sites.

TYPE OF SAMPLE	LOCALIZATION	TISSUE TYPE AND ANIMAL SPECIES	DDTs[a]	HCHs[b]	HCB	Drins[c]	Endosulfan[d]	Chlordanes[e]	Units	Reference
Penguin tissues	Brazilian Research Station Feraz, King George Island	Penguins (Adelie penguin, Papua penguin and Gentoo penguin) fat	370	12.3	373	26.4	-	73.5	ng/g lipid weight	(Taniguchi et al., 2009)
	Signy Island	Adélie penguin liver	0.002-0.028	-	-	-	-	-	µg/g	(Tatton and Ruzicka, 1967)
		Adélie penguin blubber	0.013-0.054	-	-	-	-	-		
		Adélie penguin abdominal fat	0.035-0.059	-	-	-	-	-		
	Lenie Field Station, King George Island	Adélie penguin blood	-	-	5–7.4	-	-	-	ng/g wet weight	(Corsolini et al., 2007)
		Chinstrap penguin blood	-	-	0.001–9	-	-	-		
		Gentoo penguin blood	-	-	2.8–4.9	-	-	-		
	Cape Shirreff	Chinstrap penguin blood	6.90	-	0.79	-	7.72	-	ng/g wet	(Jara-Carrasco et al., 2015)

TYPE OF SAMPLE	LOCALIZATION	TISSUE TYPE AND ANIMAL SPECIES	DDTs[a]	HCHs[b]	HCB	Drins[c]	Endosulfan[d]	Chlordanes[e]	Units	Reference
	Kopaitic Island	Chinstrap penguin blood	7.34	-	0.85	-	3.98	-	weight	
	Narębski Point	Chinstrap penguin blood	3.19	-	0.90	-	5.50	-		
Penguin eggs	Livingstone Island	Adélie penguin eggs	23 ± 10	-	7.63 ± 1.8	-	-	-	ng/g wet weight	(Schiavone et al., 2009)
		Chinstrap penguin eggs	17 ± 15	-	3.8 ± 3.7	-	-	-		
		Gentoo penguin eggs	15 ± 9	-	3.7 ± 3.5	-	-	-		
	Signy Island	Adélie penguin eggs	0.019-0.044	-	-	0.003-0.008	-	<LOD	µg/g	(Tatton and Ruzicka, 1967)
	Polish Antarctic Station Arctowski, King George Island	Adélie penguin eggs	49.6–137	-	110–208	-	-	-	ng/g lipid weight	(Mello et al., 2016)
	Chabrier Rock, King George Island	Chinstrap penguin eggs	62.5–338	-	70.1–191	-	-	-		
	Lenie Field Station,	Gentoo penguin eggs	36.4–120	-	110–	-	-	-		

TYPE OF SAMPLE	LOCALIZATION	TISSUE TYPE AND ANIMAL SPECIES	DDTs[a]	HCHs[b]	HCB	Drins[c]	Endosulfan[d]	Chlordanes[e]	Units	Reference
	King George Island				183					
Other bird tissues	Brazilian Research Station Feraz, King George Island	Brown skua fat	11958	1.22–3.11	573	254	-	1385	ng/g lipid weight	(Taniguchi et al., 2009)
		Antarctic tern fat	1001	<0.12–2.60	601	<0.48–23.0	-	124.8		
		Blue-eyed shag fat	746	1.33	161	<0.48	-	3.05		
		Snowy sheathbill fat	909	<0.12	282	22.4		179.3		
	Signy Island	Brown skua liver	1.12-4.33	-	-	<LOD	-	0.035-0.1	µg/g	(Tatton and Ruzicka, 1967)
		Brown skua fat	6.69-28.50	-	-	<LOD	-	0.120-0.730		
		Blue-eyed shag fat	0.063-0.163	-	-	0.004-0.006	-	<LOD		
Other bird eggs	Punta Hennequin, King George Island	South polar skua eggs	222–4570	-	20.5–224	-	-	-	ng/g lipid weight	(Mello et al., 2016)
Pinniped tissues	Livingstone Island	Antarctic fur seal (*Arctocephalus gazella*) blubber	<LOD	-	<LOD	-	-	-	ng/g wet weight	(Schiavone et al., 2009)

TYPE OF SAMPLE	LOCALIZATION	TISSUE TYPE AND ANIMAL SPECIES	DDTs[a]	HCHs[b]	HCB	Drins[c]	Endosulfan[d]	Chlordanes[e]	Units	Reference
		Antarctic fur seal (*Arctocephalus gazella*) liver	191 ± 106	-	2.2 ± 0.88	-	-	-		
		Antarctic fur seal (*Arctocephalus gazella*) muscle	103 ± 55	-	1.37 ± 0.69	-	-	-		
	King George Island	Crabeater seal (*Lobodon carcinophagus*) fat	14.4	0.223	7.23	18.4	2.09	22.8	ng/g lipid weight	(Cipro et al., 2012)
		Antarctic fur seal (*Arctocephalus gazella*) fat	168	3.21	4.72	82.4	21.15	78.2		
		Weddell seal (*Leptonychotes weddellii*) fat	131	2.59	5.77	18.5	14.0	9.5		
		Southern elephant seal (*Mirounga leonine*) liver	98.7	1.41	7.48	6.88	2.72	37.7		

TYPE OF SAMPLE	LOCALIZATION	TISSUE TYPE AND ANIMAL SPECIES	DDTs[a]	HCHs[b]	HCB	Drins[c]	Endosulfan[d]	Chlordanes[e]	Units	Reference
	Elephant Island	Southern elephant seal	187.72	1.905	9.89	10.205	2.85	37.28	ng/g lipid weight	(Miranda-Filho et al., 2007)
	Cape Shirreff Field Station	Antarctic fur seal (*Arctocephalus gazella*) blubber	5.66	44.27	109.59	10.77	7.01	45.60	ng/g lipid weight	(Vergara et al., 2019)
		Southern elephant seal blubber	<LOD	19.88	12.88	26.08	0.76	6.71		
	Cape Shirreff Field Station and Gabriel Gonzalez Videal Station	Weddell seal (*Leptonychotes weddellii*) blubber	7.6-17.81	48.96-75.41	94.57-340.66	34.72-42.13	0.70-3.88	37.87-106.17		
		Leopard seal blubber	5.51-7.29	49.75-76.07	81.15-95.45	15.01-31.18	0.12-4.65	35.65-62.88		
		Crabeater seal (*Lobodon carcinophagus*) blubber	<LOD	75.70-111.15	72.86-311.39	14.76-61.60	<LOD-3.72	50.10-52.66		
Aquatic	Signy Island	Notothenia - fish	0.008-0.033	-	-	0.001-	-	0.002-0.004	µg/g	(Tatton and

TYPE OF SAMPLE	LOCALIZATION	TISSUE TYPE AND ANIMAL SPECIES	DDTs[a]	HCHs[b]	HCB	Drins[c]	Endosulfan[d]	Chlordanes[e]	Units	Reference
organisms						0.009				Ruzicka, 1967)
tissues	Potter Cove, King George Island	*Notothenia coriiceps* (mean in muscle, liver, gonads, gills) - fish	11.9(muscle); 14.7(liver); 13.3(gonads); 14.3(gills)	3.40(muscle); 1.29(liver); 18.0(gonads); 9.21(gills)	-	-	-	-	ng/g lipid weight	(Lana et al., 2014)
		Notothenia rossii (sum in muscle, liver, gonads, gills) - fish	253.6	49.03	-	-	-	-		
		Trematomus newnesi (sum in muscle, liver, gonads, gills) - fish	54.2	31.9	-	-	-	-		
	Weddell Sea	*Chionodraco hamatus*	12	0.94	7.9	-	-	-	ng/g lipid weight	(Strobel et al., 2018)
		Trematomus loennbergii	2.9	4.83	3.1	-	-	-		
	King George Island	*Nacella concinna* soft tissue	<LOD–1.27	1.6–3.19	<LOD–8.56	<LOD-1.11	<LOD	2.37–3.94	ng/g wet weight	(Cipro et al., 2013)
		Euphausia superba	0.05–0.79	0.14–0.35	<LOD –	<LOD-	<LOD	<LOD-0.13		

TYPE OF SAMPLE	LOCALIZATION	TISSUE TYPE AND ANIMAL SPECIES	DDTs[a]	HCHs[b]	HCB	Drins[c]	Endosulfan[d]	Chlordanes[e]	Units	Reference
					0.06	0.44				
		Notothenia spp. muscle	<LOD-11.7	<LOD-0.57	<LOD-0.06	<LOD	<LOD-0.203	<LOD-1.49		
Other	Ardley Island	Gentoo penguin droppings	1.49	2.67	-	-	-	-	ng/g	(Sun et al., 2006)
	Signy Island	Adélie penguin stomach contents	0.001	-	-	0.001	-	<LOD	µg/g	(Tatton and Ruzicka, 1967)

[a] DDTs : p,p'-DDE; o,p'-DDT; p,p'-DDD; p,p'-DDT

[b] HCHs: α-HCH; β-HCH; γ-HCH

[c] Drins: aldrin, dieldrin, endrin and isodrin

[d] Endosulfans: α-endosulfan; β-endosulfan

[e] Chlordanes: α- and γ-chlordane, oxychlordane, heptachlor, and heptachlor epoxide

LOD - limit of detection

4. Possible consequences of the presence of organochlorine pesticides for Antarctic fauna

Contemporary research (Mello et al., 2016; Strobel et al., 2018; Vergara et al., 2019) continues to show the presence of OCPs at various Antarctic trophic levels, despite the efforts to reduce their emissions. Climate conditions in Antarctica favour the persistence of OCPs. Several publications (Schiavone et al., 2009; Cipro et al., 2012; Lana et al., 2014) have highlighted the fact that Antarctic animals bioaccumulate and biomagnify these pollutants and can pass them on to their offspring. As mentioned previously, OCPs have a high affinity for fat, which acts as energy storage in the cold climate. This makes the southern polar food network especially sensitive to such contaminants. Figure 4 shows a diagram of the OCPs circulation in the abiotic environment, which then impacts the aquatic and semi-aquatic living organisms.

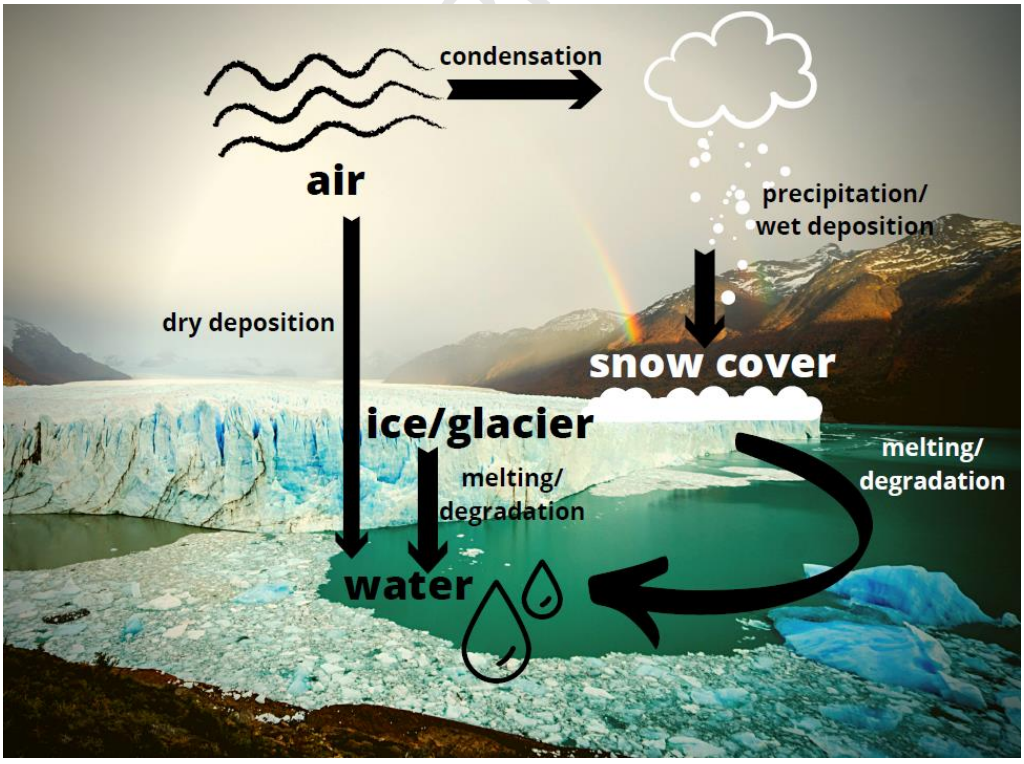


Figure 4. Diagram of OCPs circulation in the Antarctic environment. The project was created based on publications collected in Tables 1 and 2.

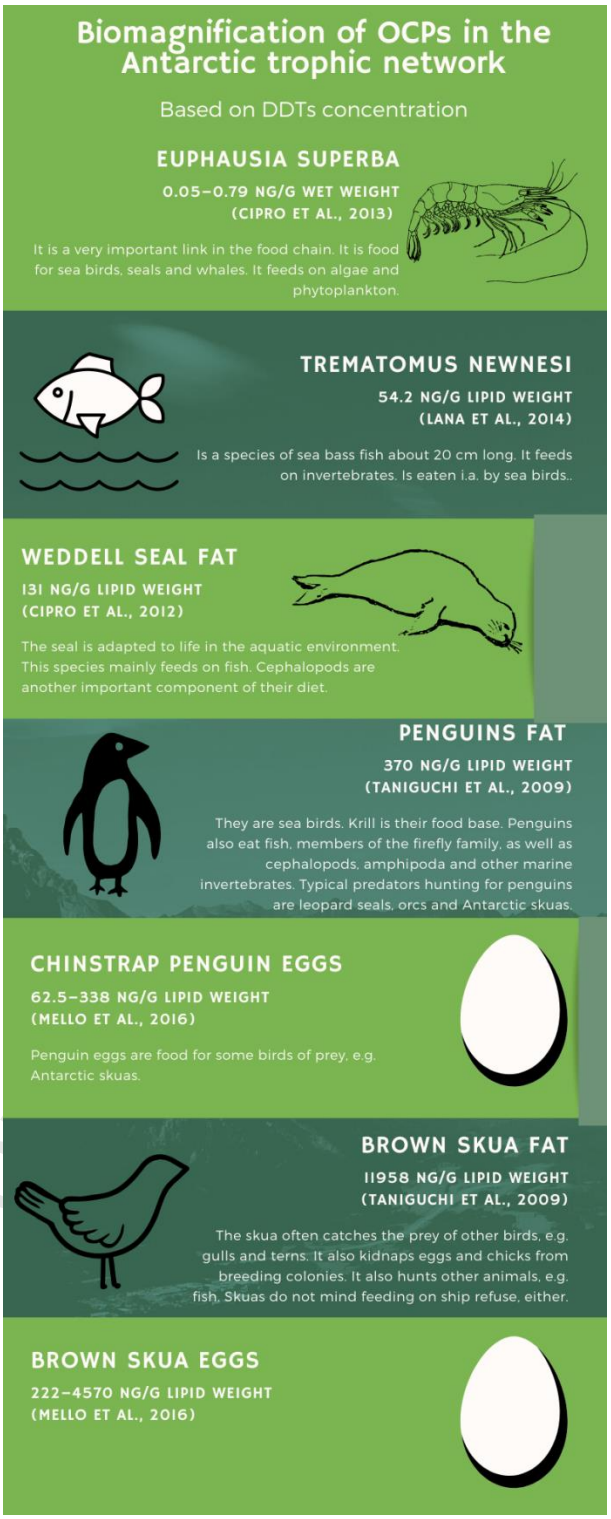
Due to biomagnification, top predators are particularly vulnerable to OCP contamination (Schiavone et al., 2009). For example, seabirds whose main food is fish have higher OCP contents in their tissues compared to non-predatory species. A further factor deteriorating the birds resistance to xenobiotic compounds is their poor ability to metabolize those (Corsolini et al., 2007). Figure 5 shows the most widespread animals on King George Island (South Shetland Islands, Marine Antarctica). The most common sea birds are penguins which are an important element of both marine and terrestrial ecosystem of the Antarctic. They mainly eat krill, but also include fish in their diet depending on the availability of food (Olmastroni et al. 2000). Adélie penguins eat up to 99% of krill. Penguins, like other birds of prey, are characterized by a higher content of OCPs and a lower level of detoxification of the body (Corsolini et al., 2007) than lower trophic level organisms, since birds cannot remove xenobiotics during gas exchange (breathing) and dermal diffusion. The removal of harmful substances can only happen through excretion and biotransformation (Goerke et al. 2004). Compared to krill, Weddell seal and southern elephant seal, which mainly feed on fish and cephalopods, show stronger biomagnification, by up to two orders of magnitude (Goerke et al. 2004).

Figure 5. Selected examples of the most common animal species on King George Island (South Shetland Islands, Marine Antarctica). Pictures were taken by J. Potapowicz during a scientific expedition to the Polish Antarctic Station in 2019.

Tanabe et al. (1987) showed that POPs are transported from mammals' fat to offspring along with their mother's milk, due to their good fat solubility. Since the milk of marine mammals is extremely high in lipids, juveniles are particularly vulnerable to POPs exposure. The Antarctic fur seal milk can be up to 39.8% fat (Goldsworthy and Crowley, 1999). Nakashima et al. (1997) found that in addition to breastfeeding, mammals are exposed to the penetration of POPs into their bodies through the uterus before birth. Other studies (Pastor et al., 1995; Drouillard and Norstrom, 2001) claim that the concentrations of contaminants including OCPs in the eggs of waterbirds correspond to those in maternal tissues. Considering these relationships, it is considered that if developing embryos are exposed to the same POPs concentration as mature individuals, and are more susceptible to chemical pollution, we will most likely observe toxic effects (Schiavone et al., 2009). Figure 6 A presents the biomagnification process on the example of the sum of DDTs in the tissues and eggs of Antarctic animals. In addition, Figure 5 B shows a food network occurring between the described Antarctic environment animals (Fig. 6 A).

Fish can biotransform p, p′-DDT into a stable metabolite, p,p′-DDE, and on this basis it can be determined when DDT has entered the aquatic environment (Vives et al., 2005). This means that the higher the p, p′-DDE / DDT ratio, the earlier the DDT had been emitted into the environment (Yogui et al., 2003). Based on this ratio, van den Brink et al. (2011) showed that p,p′-DDE concentration levels proportionally decrease in Antarctica pelagic organisms, while they increase in benthic organisms, which suggests a fresh input of contaminants into the pelagic biota, while the concentrations in benthic organisms approximate the total environmental burden of OCPs in Antarctica.

A.



B.

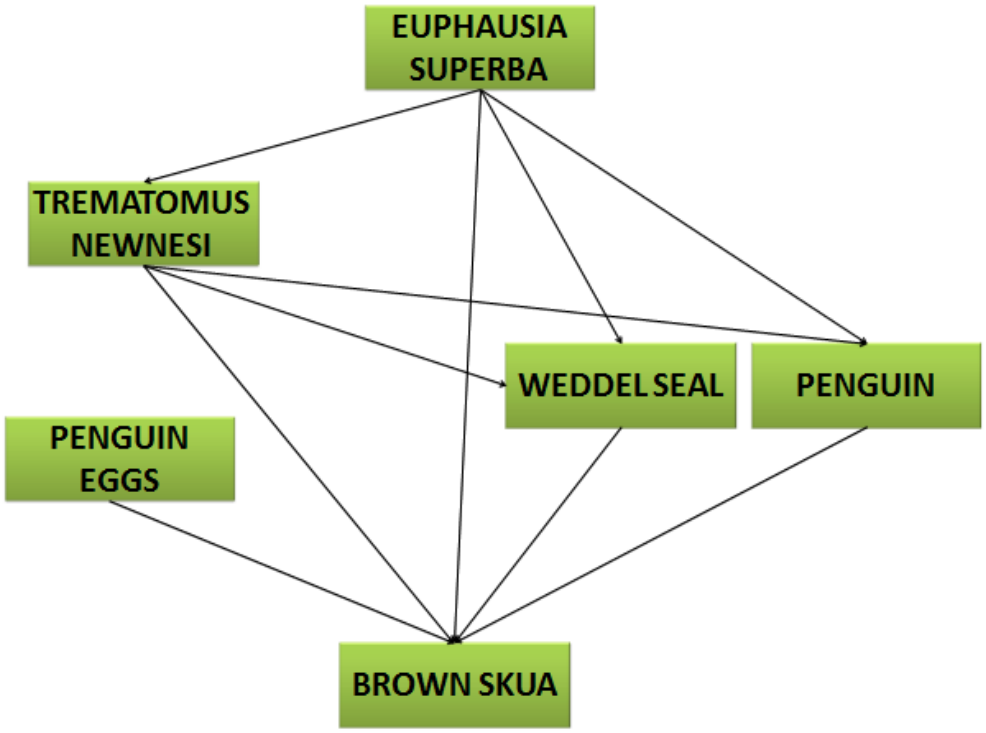


Figure 6. A. Biomagnification process on the example of DDTs in tissues and eggs of Antarctic animals. B. An example of a food network occurring in the Antarctic environment in which biomagnification of OCPs is possible.

The HCH isomers are characterized by different properties which affect environmental stability and biodegradation of each of them (Phillips et al., 2005). For example, it was found that the α-HCH isomer bioaccumulates, while the β-HCH is stable to enzymatic degradation, making it more persistent in biota and more likely to biomagnify (Cipro et al., 2010; Tanabe et al., 1997). Based on the levels of HCH isomers in fish tissues, it was discovered that gonads are the main organ in which HCHs accumulate, which is a threat to the reproductive system (Lana et al., 2014). In addition, during the reproductive phase of catfishes and carps, these compounds are transported from the liver to the ovary, which results in reproductive disorders (Singh and Singh, 2008).

Based on POPs concentrations in the tissues of seabirds, it was concluded that the exposure to these chemicals in the Antarctic ecosystem decreased reproduction and survival rates, while it also increased the parasitic load (Sagerup et al. 2000, Bustnes et al. 2003, 2004). Other noted impacts were an increased asymmetry of the wings and the occurrence of immunohematological disorders. Moreover, it was found that organochlorine pollutant loads can determine the proliferation of

leukocytes in glaucous gulls (Henriksen et al., 2000). Grasman and Fox (2001) showed that significant concentrations of POPs may cripple the immune system cells functioning, consequently leading to an intensification in the production of these cells to compensate and fight back against low tier infections. The final effects of the described POPs-induced immunosuppression are infections, a disruption in the production of heterophile antibodies and lymphocytes (Grasman, 2002; Bustnes et al. 2004), and an increased exposure to parasitic diseases (Sagerup et al. 2000).

5. Conclusions

OCPs occur in Antarctic waters and biota and constitute a threat to the proper functioning of aquatic organisms. OCPs are characterized by a long residence time in the Antarctic environment, thus they persist even after a long period following emission. The reason for this are the properties of OCPs: slow degradation and the ability to accumulate in the Antarctic environment. As a result of climate change, there may also be secondary effects: accumulation of these chemicals in the Antarctic regions affected by temporary cooling and their reemission in the warming areas.

The most commonly detected OCPs in the Antarctic environment are DDTs, HCHs, HCB, aldrin, dieldrin, endrin, isodrin and chlordanes. The presence of OCPs was identified in various aquatic environments of the Antarctic (seawater and polynya water, freshwater, porewater, snow, firn and ice) and significant concentrations were found in biota. The presence of OCPs was confirmed in multiple tissues of aquatic organisms, bird eggs, and the content of the digestive tract of animals at higher trophic levels. Both OCPs and their degradation products negatively affect the living organisms in Antarctica, disrupting the natural ecosystem.

Due to the accumulation of OCPs in the abiotic and biotic environment in the Antarctic, it is necessary to monitor the concentration of this class of pollutants. The persisting knowledge gaps concern mapping the sources of these anthropogenic pollutants, including the secondary accumulations in the environment, and their transmission pathways between individual elements of the environment. Only such comprehensive recognition of the OCPs emissions into the Antarctic environment would allow to limit their impact, which depends on the long-term organism exposure to

these compounds. As a global problem, finding its solutions will depend also on how effective are the legal regulations on the use of OCPs worldwide.

Acknowledgements

The article was created partly thanks to funding by the European Union Funds from the project POWR.03.02.00-IP.08-00-DOK/16. This study was also partially funded by the National Science Centre of Poland grant NCN 2017/26/D/ST10/00630 awarded to K. Koziol. The inspiration to create this work was research conducted on the Henryk Arctowski Polish Antarctic Station under the agreement between the Institute of Biochemistry and Biophysics, Polish Academy of Science (IBB, PAS), and Gdańsk University of Technology.

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Declaration of competing interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: